Decontamination of Beryllium Solution from Iron by 1,10-Phenanthrolin Ligand-Ion Flotation

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ABSTRACT

The main target of the study was focused on the process of eliminating the major cationic species co-existed with natural processed Be solution such as Be, Fe and Al. The cations may be eliminated or decreased via their concentration as ionic species by chelation or precipitation heavy metal ions in 100 ml samples were first chelated, in their synthetic single element solution, with 1,10-phenanthroline with different concentrations at different pH values then floated with the aid of sodium lauryl sulfate (SLS) with different concentrations and rate of addition of nitrogen bubbles. The data of the resulted experimental work for different aforementioned factors (pH, chelate conc. collector conc. and rate of addition finally nitrogen gas flow rate and flotation time).

Key Words: Ion Floatation/ Beryllium/ Iron/ 1,10-Phenanthrolin/ Sodium Lauryl Sulfate.

INTRODUCTION

Ion flotation is a comparatively novel separation technology, that uses special properties found in the interfaces in order to concentrate ions or other species with electric charge contained in aqueous solutions (1). First described by Sebba in (1959)(2), for recovering and removing metal ions from dilute aqueous solutions (3–6). This process involves the removal of surface inactive ion species from aqueous solution by adding the proper long chain surface active agent of opposite charge to the ion to be separated. A surface active reagent, known as a collector, is added to the solution to be treated and adsorbs at the solution–gas interface. After the subsequent passage of gas bubbles through the solution, surfactant and ions are accumulated at the gas/liquid interfaces and are carried into a foam or froth, rising above the solution. The froth is swept from the top of the flotation cell. Appropriate surfactants prevent bubble rupture and promote the formation of foam (7). Ion flotation covers two main application fields: recovery of valuable material and water decontamination (8).

Precipitate flotation involves firstly the immobilization of ions as precipitates, e.g. by raising the respective concentrations may lead to precipitation of the ion as a surfactant floatable product, before air is passed. This means that it is not a solution anymore but rather dispersion (9, 10).

MATERIALS AND METHODS

Reagents and Solutions

All chemicals used in this study were of analytical-reagent grades. All aqueous solutions were prepared in double distilled water. Take 1000ml of sample into a beaker add 2ml of (1+1) sulphuric acid, 2-5ml of 10% hydroxylamine sulphate (reducing agent) and 1-4ml of 0.01M1-10- phenanthroline (chelating agent) solution, add 1ml of 1% sodium lauryl sulphate (SLS). Collect the foam coming out
of the separator in a 50ml beaker which contained 2ml of 1-propanol as a foam breaker, pH of the solutions during experiments was adjusted with 6M ammonium.

**Apparatus**

Ion Flotation Machine (a cylindrical tub of 13 cm length and 4.5 cm inner diameter, provided with a stopcock at the bottom and a stopper at the top). The pH-values of the solutions were measured using WTW inolab level 1. The residual Al\(^{3+}\) ion content in mother liquor was analyzed by AAS supplied with acetylene and nitrous oxide burner heads at 309.3 nm.

![Photo (1) Ion Flotation Machine](image)

**Procedure**

According to the recommended procedure for low iron concentration separation by ion floatation after chelation with 1-10- phenanthroline (chelating agent), 1000ml of sample was take into a beaker add 2ml of (1+1) sulphuric acid, 2-5ml of 10% hydroxylamine sulphate (reducing agent) and 1-4ml of 0.01M chelating agent solution. Adjust the PH 2-8 with 6M ammonium and stirr the solution for 10min. Pour the solution into the foam separation tube to which nitrogen gas is being fed at a low flow rate. After adjusting the nitrogen gas flow rate to 150ml\(\times\)min add 1ml of 1% sodium lauryl sulpha te (SLS) aqueous solution from the top of the separation and at the same time start feeding the 1% SLS solution through the lower side tube at the flow rate starting from 0.1ml\(\times\)min. to 0.3ml\(\times\)min. collect the foam coming out of the separator in a 50ml beaker which contained 2ml of 1-propanol as a foam breaker. Continue the separation for 20 min. in different intervals measure the metal contents in the solutions obtained. A series of chelation-floatation experiments were carried out to find out the effect of pH, amount of chelating agent sufficient for iron present, rate of floating agent flow time of floatation and rate of gas flow.

The floatability (F) of Fe(III) was determined from the relationship:

\[
F = \frac{(C_i - C_f)}{C_i} \times 100\%
\]

where, \(C_i\) and \(C_f\) denote the initial and final concentrations of Fe(III) ion in mother liquor. All experiments were carried out at room temperature, \((20 \pm 1^\circ C)\).

**RESULTS AND DISCUSSION**

A series of chelation-floatation experiments were carried out to find out the effect of pH, amount of chelating agent sufficient for iron present, rate of floating agent flow time of floatation and rate of gas flow.

**Effect of pH**

The hydrogen ion concentration has a significant effect on the formation of chelate and on the floatation process. From all the data of experiments of 5, 10, 15, 20 minutes floatation it is clear that floatability of iron increased markedly in the pH range 4-6 specially in the higher ion concentration experiments. Figs. (1-8) represent the relation between pH variation with other parameter variations under certain circumstances, such as amount of chelating agent (1, 2, 3 and 4ml), time of floatation, rate of SLS flow and gas flow.
Fig. (1): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at 1ml chelating agent.

Fig. (2): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at 2ml chelating agent.
Fig. (3): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at 3ml chelating agent.

Fig. (4): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at 4ml chelating agent.
**Fig. (5):** Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at 1ml chelating agent.

**Fig. (6):** Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at 2ml chelating agent.
Fig. (7): Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at 3ml chelating agent.

Fig. (8): Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at 4ml chelating agent.
Reducing Agent, Chelating Agent and Ion Concentration Effect

All previous work on iron apply 5ml of 10% hydroxyl amine sulphate as a reducing agent while in this case, 2ml of reducing agent proved to be enough to reduce Fe(III) present in solution. Further, 3ml of 1,10-phenanthroline solution was shown to be sufficient for qualitative results specially with higher ion concentration (0.004% and 0.005%) the effect of the amount of chelating agent, added (1, 2, 3 and 4ml) correlated with different ion concentration (0.003, 0.004 and 0.005%) was declared from Figs. (9-14). The Figures prevailed that floatability of the ion increased with chelating agent amount increase under all different conditions till nearly constant value after 3ml of the reagent.

Fig.(9): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at 0.003%Fe and different chelating agents.
Fig.(10): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at 0.004% Fe and different chelating agents.

Fig.(11): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at 0.005% Fe and different chelating agents.
Fig. (12): Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at 0.003% Fe and different chelating agents.

Fig. (13): Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at 0.004% Fe and different chelating agents.
Fig. (14): Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at 0.005% Fe and different chelating agents.

Effect of Floatation Time

The effect of separation time was also examined. Results are presented in Figs. (15-20) as shown from them maximum and quantitative recoveries were attained after 15 min. which chosen for separation time by floatation. From figures one can confirm that the floatability of the ion increased with the time of floatation till certain limit under all variable parameters of pH, rate of SLS flow, chelate addition, ion concentration and gas flow.
Fig. (15): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at pH (4, 5, 6 and 7) at 0.003% Fe.

Fig. (16): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at pH (4, 5, 6 and 7) at 0.004% Fe.
Fig. (17): Fe percent recovery with 1% SLS, flow rate of 0.1 ml/min. and nitrogen flow rate 100 ml/min. at pH (4, 5, 6 and 7) at 0.005% Fe.

Fig. (18): Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at pH (4, 5, 6 and 7) at 0.003% Fe.
Fig. (19): Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at pH (4, 5, 6 and 7) at 0.004% Fe.

Fig. (20): Fe percent recovery with 1% SLS, flow rate of 0.2 ml/min. and nitrogen flow rate 150 ml/min. at pH (4, 5, 6 and 7) at 0.005% Fe.
d) Effect of SLS and nitrogen gas flow rate

The data I Figs. (1-4) under certain experiments conditions have a relative one under the same conditions except for the floating agent (1% SLS) flow rate and bubbling gas (Nitrogen) flow rate which represented in Figs. (5-8). The former results of Figs. (1-4) were carried out at slow flow rate for both solution and gas while a faster flow rate was that most of the ion floatability results were shifted to their corresponding higher values under the same conditions and this can be concluded easily when comparing them during Figs. (21-24). It was clearly that, 0.2 ml/min. 1% SLS flow rate during 15 min. with 150 ml/min. nitrogen gas flow were the most promising rates of solution and gas flow, respectively. Faster rates may collapse and disturb the floatation system and didn't give higher promising floatability results. For the addition of 1% SLS solution, it was necessary to add both from the top at the beginning and continuously from the bottom, because several large scums which might be originated from [Fe(phen)]^{2+} (Ls) remains on the surface of the separator and prevented the quantitative floatation in case of addition from the top during all the experiment while N2 gas for inert atmosphere to prevent Fe oxidation.

Fig. (21): Fe percent recovery with 1% SLS, flow rate of 0.1 and 0.2 ml/min. and nitrogen flow rate 100 and 150 ml/min. at 1ml chelating agent and different pH's.
Fig. (22): Fe percent recovery with 1% SLS, flow rate of 0.1 and 0.2 ml/min. and nitrogen flow rate 100 and 150 ml/min. at 2ml chelating agent and different pH’s.

Fig. (23): Fe percent recovery with 1% SLS, flow rate of 0.1 and 0.2 ml/min. and nitrogen flow rate 100 and 150 ml/min. at 3ml chelating agent and different pH’s.
Fig. (24): Fe percent recovery with 1% SLS, flow rate of 0.1 and 0.2 ml/min. and nitrogen flow rate 100 and 150 ml/min. at 4ml chelating agent and different pH’s.

**Floatability of Beryllium**

To find out the effect of chelation – floatation by 1,10-phenanthroline and SLS, respectively on beryllium ion in this target to purify beryllium concentrates by ion flotation, the most promising iron concentration and separation by ion floatation, conditions were applied on a synthetic single beryllium solution containing 0.06% Be (600 ppm) which resample the solution concentration produced from part (I) of Al elimination. The experiment was carried out at different pH’s. 4, 5, 6 and 7 for 15 min. flotation time with 0.2ml / min. 1% SLS solution flow rate and 150ml / min. nitrogen gas flow rate after 3ml 1, 10-phenanthroline addition. The results were 0.17%, 0.19%, 0.25% and 0.25% Be lose (floatation percent) at pH 4, 5, 6 and 7, respectively.

**Floatability of Authentic Be and Iron Mixture**

A synthetic mixture containing Be and Fe resample the naturally prepared one after Al separation by precipitate – floatation in part (I) was brought into a flotation experiment for chelation and chelate separation by SLS in the previously determined optimum conditions. The results were cleared in Table(1).

It is clear that the presence of forgien ion (ionic strength) floatability of iron after chelation especially when the added ion (Be) don’t form chelate easily with 1,10-phenanthroline and couldn't floated by the present method.
Table (1): percent floatability of Be and Fe at different pH’s.

<table>
<thead>
<tr>
<th>Ions</th>
<th>pH</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>%</td>
<td>0.2</td>
<td>0.21</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Fe</td>
<td>%</td>
<td>90</td>
<td>95</td>
<td>97</td>
<td>98</td>
</tr>
</tbody>
</table>

Case study (Umm sleimat beryl concentrate)\(^{(1)}\)

Partially purified beryllium concentrate produced after Aluminum elimination in the first part of the work via flotation cell of the precipitate flotation containing mainly beryllium with 0.005% iron was subjected to the optimum chelate flotation conditions of the present part to be decontaminated from iron. It was found that only about 90% of the iron can be concentrated and separated in the foam while no more than 1% lose in Be content was attained. The depress in the iron floatability my be attributed to the ionic strength effect of some metals which form chelates easily with 1,10-phenanthroline and floated by the present method such as Mn (II) ions which also quantitatively floated at the same pH range as iron. When 4ml of chelating agent was added and 0.3ml/min 1% SLS flow rate is applied iron floatation percent reached to more than 98% summarized flow diagram of the process is presented in Fig.(25).

![Fig.(25): Schematic diagram for the Chelate flotation of Fe from beryl solution of Umm Sleimat area. (Barially mass balanced).](image-url)
REFERENCES

(2) F. Sebba; Nature; 184, 1062 (1959).